Development of Complex Hydride Hydrogen Storage Materials and Engineering Systems

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Objectives

Hydrogen Storage Engineering Systems Research

- Develop 1-D, 2-D and 3-D models for metal and complex hydride hydrogen storage systems
- Calibrate models using Savannah River Technology Center metal hydride hydrogen storage system
- Develop user friendly software package for metal hydride hydrogen storage system design optimization and scale-up

Complex Hydride Hydrogen Storage Materials Research

- Study effect of metal dopants, proprietary additive, and Al powder on dehydrogenation and rehydrogenation of $NaAlH_4$
- Compare dehydrogenation kinetics of un-doped and Ti-doped $NaAlH_4$, LiAlH4, and $Mg(AlH_4)_2$.
- Initiate Raman and other spectroscopic and molecular modeling analyses for fundamental understanding of dopant and other additives.

2004 FY Budget

- Total Funding (18 mo Period Beginning 06/06)
  - $335,000 + $83,759 cost share
- Personnel
  - PI: 1.35 academic and 2 summer months
  - Research Professor: 8.5 calendar months
  - Postdoctoral Associate: 9 calendar months
  - Two PhD Students plus Tuition: 36 calendar months
- Travel
- Materials and Supplies

Technical Barriers and Targets

Hydrogen Storage Material and System

DOE Targets:

2005 – 1.5 kWh/kg (4.5 wt %), 1.2 kWh/L, $6/kWh

2010 – 2 kWh/kg (6 wt %), 1.5 kWh/L, $4/kWh

2015 – 3 kWh/kg (9 wt %), 2.7 kWh/L, $2/kWh

Technical Barriers:

- higher system weight, high volume
- high cost of storage
- durability of at least 1500 cycles
- lower than expected energy efficiency
- long refueling time
- lack of availability of codes and standards
- no life cycle and efficiency analyses

Approach

- Synthesis and analysis of new and improved complex hydrides for hydrogen storage

  - effect of various preparation methods (e.g. ball milling), additives and metal dopants on the hydrogenation/dehydrogenation performance of these materials

- Mathematical model development for metal and complex hydride hydrogen storage systems

  - develop models of varying degree of complexity for accurately predicting hydrogen charge and discharge behavior from the storage bed.

  - study various geometric configurations for improving design and performance of the storage vessel

Project Safety

Complex Hydrides Synthesis

- Sodium alanate is highly flammable material. It readily reacts, with water generating flammable and explosive hydrogen gas
- Storage under nitrogen, away from air mandatory ⇒ synthesis carried out inside nitrogen glove-box
- Recent minor incident with Ti-doped $NaAlH_4$ at SNL, even when inside and Ar glove-box, reiterates the sensitivity of this material with exposure to water

Hydrogen Storage Systems Research

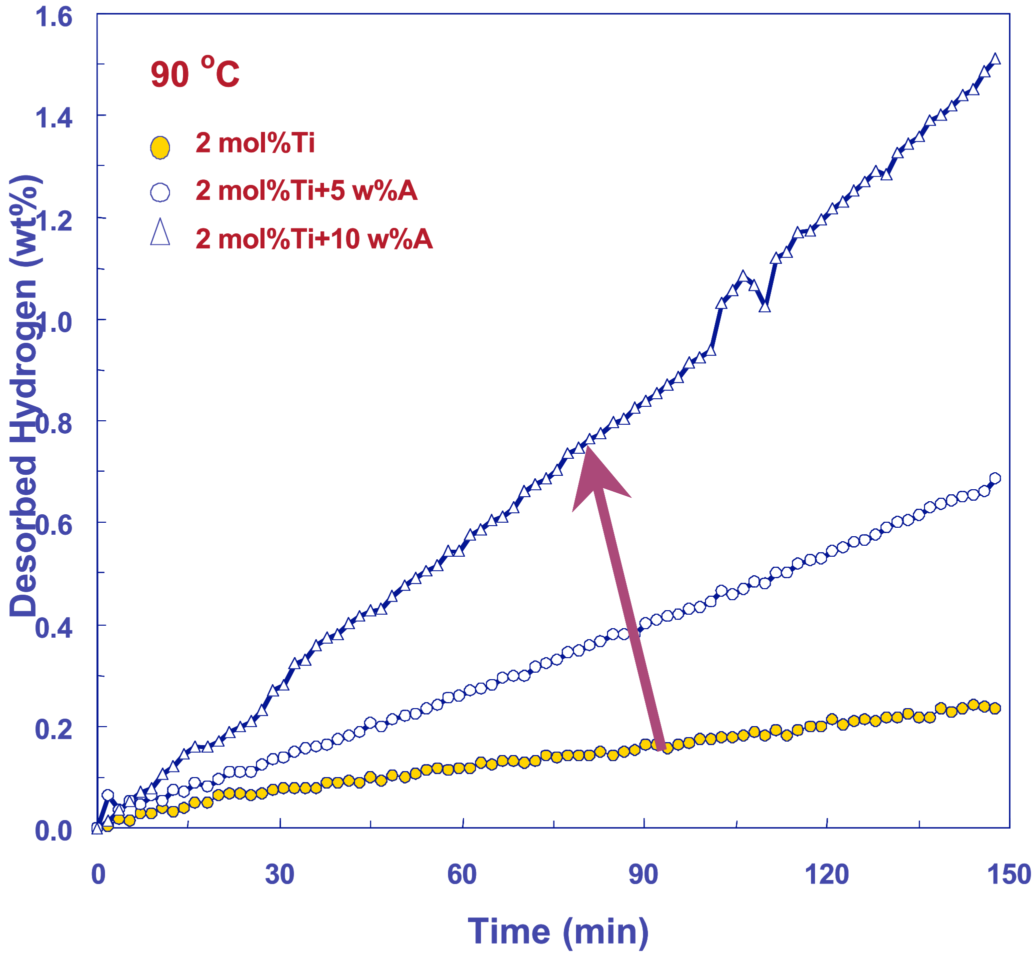
- Mischmetal alloy based hydride used for this study very stable at room temperature. Auto-ignition temperature above 500 ^{o}C. It is non-explosive at room temperature, but other metal hydrides can be explosive.
- Hydride particles undergo expansion and contraction during charge and discharge cycles. Vessel of high of enough material strength is used to withstand this stress.

Project Timeline

6/04-8/04	8/04-11/05	10/04-12/05	6/05-5/05	3/05-8/05	7/05-11/05
Phase I	Phase II	Phase III	Phase IV	Phase V	Phase VI

- Phase I: Complete analysis on the reversibility of the Ti-doped $LiAlH_4$ system
- Phase II: Complete analysis on the reversibility of the Ti-doped $Mg(AlH_4)_2$ system
- Phase III: Complete Raman and molecular modeling analyses on the Ti-doped $NaAlH_4$ system
- Phase IV: Complete analysis on the Ti-doped $NaAlH_4$ system with proprietary additive
- Phase V: Complete analysis on the effect of high temperature and pressure ball milling of complex hydrides
- Phase VI: Complete analysis on long-term cycling and scale-up of promising complex hydrides

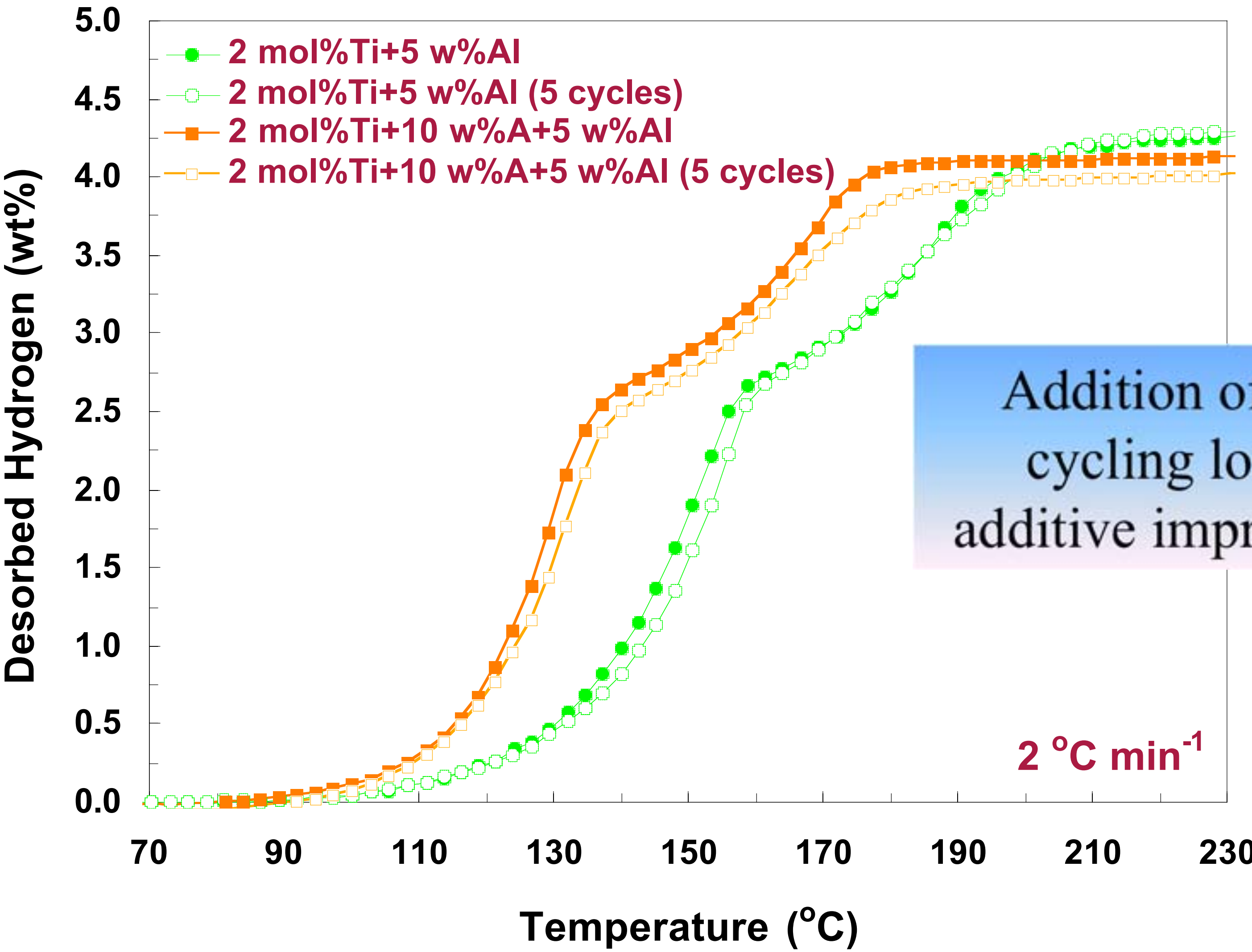
Effect of Additive Concentration on Dehydrogenation of 2% Ti-$NaAlH_4$



At 90°C, 10 wt% additive produces six fold increase in kinetics!

Best kinetics observed so far for this widely studied complex hydride!

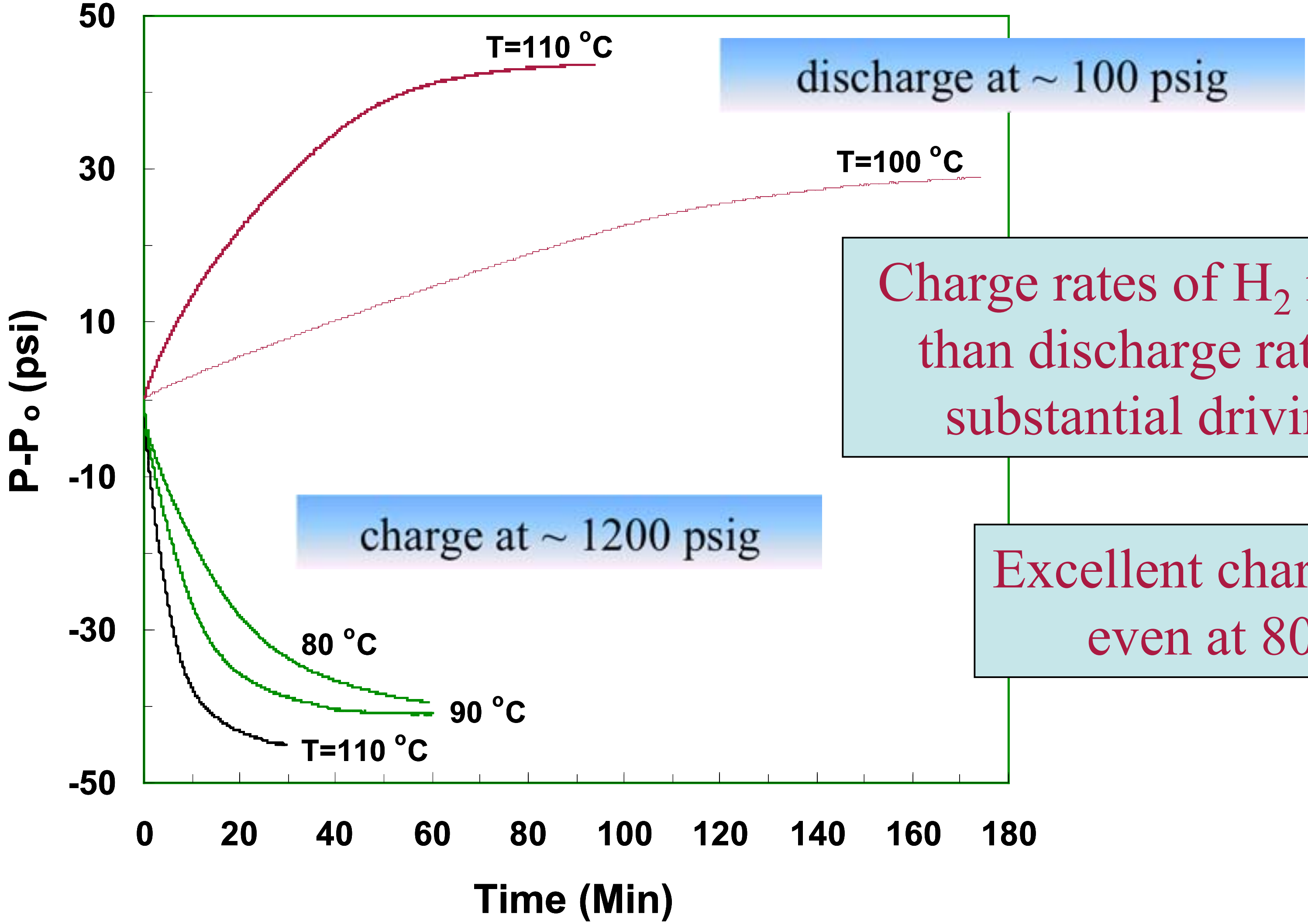
Effect of Cycling on Dehydrogenation of 2% Ti-$NaAlH_4$ with 10 wt% Additive and 5 wt% Al



Addition of Al reduces cycling losses, while additive improves kinetics!

J. A. Ritter A. D. Ebner, R. Zidan J. Wang and C. E. Holland, US Patent Pending (2004).

Qualitative Kinetics of the H_2 Charge and Discharge Process for 2% Ti-$NaAlH_4$ with 10 wt% Additive and 5 wt% Al



Charge rates of H_2 much faster than discharge rates, due to substantial driving force.

Excellent charge rates even at 80°C!

Industrial Fuel Cell Vehicle Program

Partnership

- Industrial: John Deere
- Government: WSRC/DOE
- University: USC

Onboard Metal Hydride Vessel

Metal Hydride Vessel on Vehicle

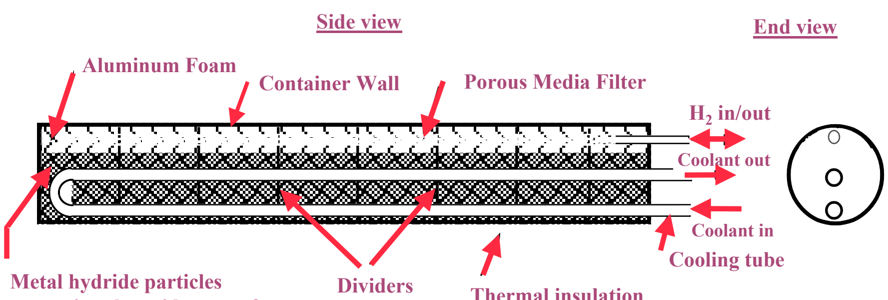
Mathematical Models

Six Systematically More Realistic Models

- isothermal equilibrium model (analytical)*
- one dimensional axial-flow*
- one dimensional axial-flow, radial-energy model (AFRE)
- AFRE model with variable conductivity
- two-dimensional
- three-dimensional

** S. A. Gadre, A. D. Ebner, S. A. Al-Muhtaseb and J. A. Ritter, Ind. Eng. Chem. Res.,42, 1713-1722 (2003).*

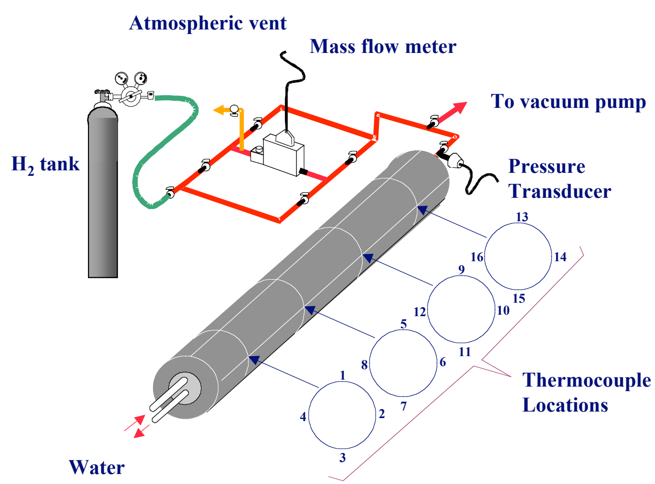
WSRC Metal Hydride Vessel Schematic*



***Patented**

Modeling and experiments based on commercially viable $Lm_{1.06}Ni_{4.96}Al_{0.04}$ metal hydride system.

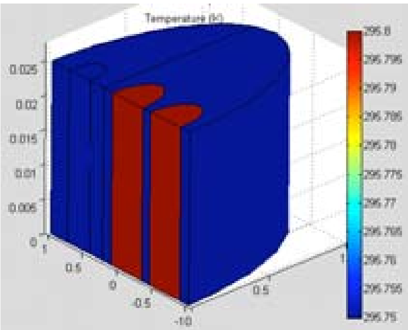
Experimental Hydrogen Storage Test Facility Layout



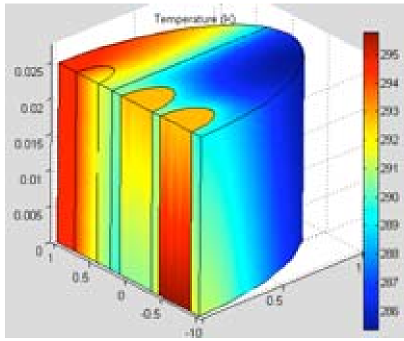
One of these tubes in the USC facility.

3-D model Predictions of the Temperature Profile Variation During Discharge

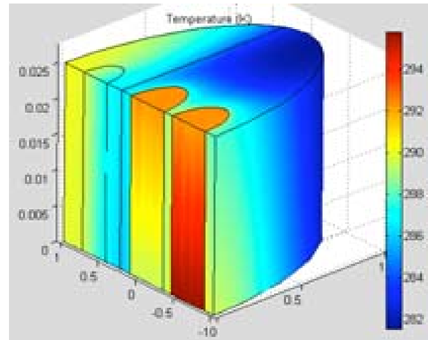
t = 0.00 hr



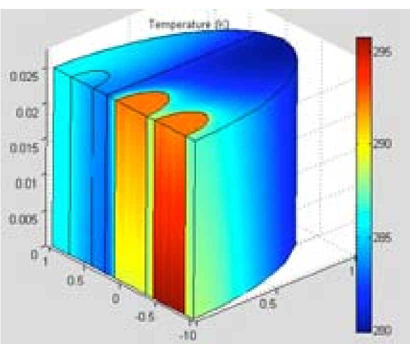
t = 0.13 hr



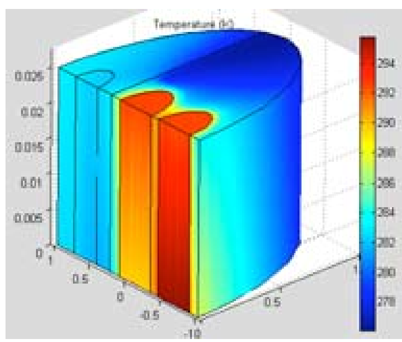
t = 0.26 hr



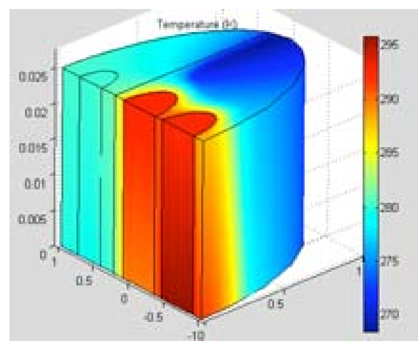
t = 0.39 hr



t = 0.52 hr



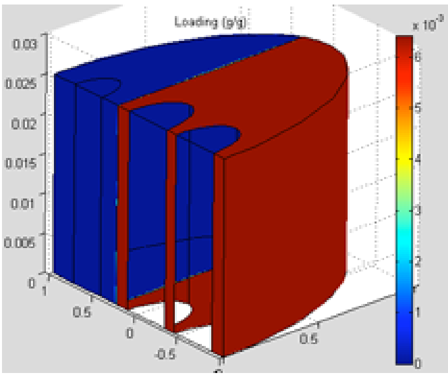
t = 0.65 hr



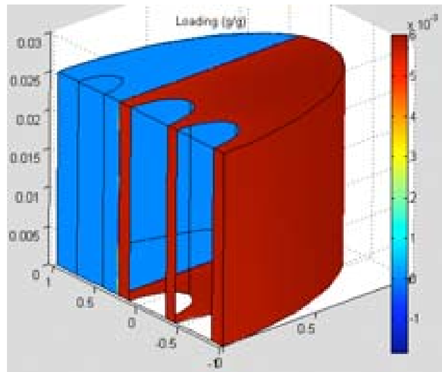
30 SLPM of hydrogen discharging from 24 atm to 1 atm in 0.65 hrs from initial temperature of 295; 295 K cooling water flowing at 0.5 gpm.

3-D Model Predictions of the Loading Profile During Discharge

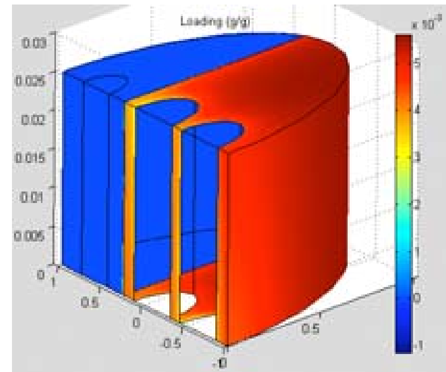
t = 0.00 hrs



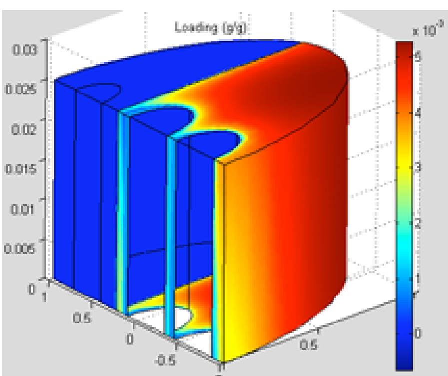
t = 0.13 hrs



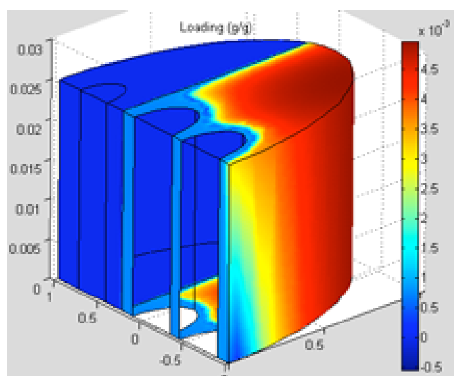
t = 0.26 hrs



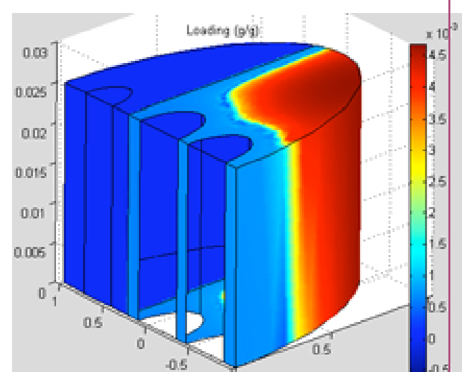
t = 0.39 hrs



t = 0.52 hrs



t = 0.65 hrs



30 SLPM of hydrogen discharging from 24 atm to 1 atm in 0.65 hrs from initial temperature of 295; 295 K cooling water flowing at 0.5 gpm.

Interactions and Collaborations

- Dr. Ragaiy Zidan, Hydrogen Technology Laboratory, Savannah River Technology Center
- Dr. Maximilian Fichtner, Karlsruhe Research Center, Germany
- Dr. Jacque Huot, Hydro-Quebec, Canada
- Professor Alexander Angerhofer, Chemistry Department, University of Florida
- Professor Ruhullah Massoudi, Chemistry Department, South Carolina State University

Fundamental Hydrogen Storage Materials Issues Being Researched

- fundamental understanding of the roles of the Ti dopant, its interaction with the additive and even the presence of adding additional Al

What else can be added and why?

- reproducible processing, i.e., ball milling is more of an art than a science

Is there a better way?

- extension of the $NaAlH_4$ research to other complex hydrides

How much effort should be devoted to what systems?

Fundamental Hydrogen Storage Systems Issues Being Researched

- thermoconductivity of the metal hydride as a function of hydrogen loading and temperature

  How do you predict this important property, especially when coupled with the metal foam?

- thermoconductivity of the metal (Al) foam heat transfer insert

  Are there better materials or structures to improve heat transfer?

- fundamental design of the metal hydride bed

  How many heat transfer tubes, in what configuration and whether to operate multiple beds in series or parallel?